

**Poly(ethylene maleate) — Cyclopentadiene: A  
Model Reactive Polymer-Vapor System for  
Evaluation of a SAW Microsensor**

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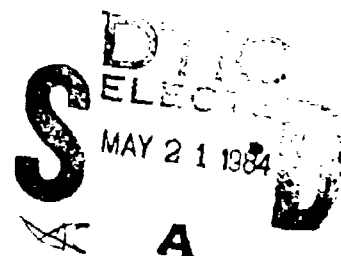
*Polymeric Materials Branch  
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April 23, 1984

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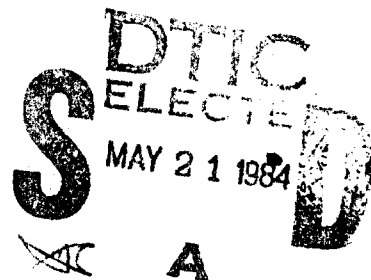
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<p>A model reactive polymer-vapor system based on the Diels-Alder reaction has been used to verify the behavior of a surface acoustic wave (SAW) device chemical microsensor. Poly(ethylene maleate) (PEM) was synthesized and characterized both spectroscopically and thermally for use as a selective receptor of cyclopentadiene vapor. The formation of a non-reversible Diels-Alder adduct between a PEM coating on a SAW delay line oscillator and the cyclopentadiene results in a film mass change which is easily measured by the SAW device. Physical absorption of nonreacting solvent vapors can be distinguished from the cyclopentadiene interaction. The resulting cyclopentadiene dosimeter is capable of detecting 200 ppm of vapor in 1 minute. Significantly lower detection limits are possible if longer vapor integration periods are allowed.</p>			
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POLY(ETHYLENE MALEATE) - CYCLOPENTADIENE: A MODEL REACTIVE  
POLYMER - VAPOR SYSTEM FOR EVALUATION OF A SAW MICROSENSOR

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INTRODUCTION

Surface acoustic wave devices offer significant potential as chemical microsensors. When used as an oscillator, a SAW delay line is extremely sensitive to small mass changes on its surface (1). To function as a vapor specific sensor, the SAW device requires a chemically sensitive and selective coating to interact with the vapor to be detected. Mass changes in the coating resulting from either physical sorption or chemical reaction of the vapor with the film, result in corresponding resonant frequency changes of the SAW delay line oscillator. Coating thicknesses approximating 1% of the acoustic wavelength are required by the SAW device in order that mass absorption capacity for vapors is high enough for good sensitivity and diffusion times are reasonably rapid, but not so thick that too much acoustic energy is absorbed from the Rayleigh wave thereby quenching the oscillation (1). For the following work at a SAW frequency of 31 MHz on ST-Quartz, this corresponds to a film thickness of 1 micrometer.

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The objective of this study was to observe the behavior of a SAW vapor sensor coated with a film having a high degree of selectivity for a particular vapor. Information regarding sensor response time, sensitivity, minimum detectable quantity, reversibility, and linearity obtained in this investigation was required to assess the potential of the SAW vapor sensing technique.

The selective coating-vapor combination selected as a model system in this study is based on the Diels-Alder reaction which occurs between a poly(ethylene maleate) (PEM) coating and cyclopentadiene vapor.

The exposure of a thin film of poly(ethylene maleate) to cyclopentadiene vapor should result in several changes. First the film should experience a small mass increase due to the physical permeation of cyclopentadiene vapor into the polymeric matrix. Second, the film should be plasticized by the vapor permeation resulting in a reduced elastic modulus of the film. Third, reaction between the film and cyclopentadiene which has permeated should result in the formation of the Diels-Alder adduct. The reaction should cause a continuous increase in the film mass (and a corresponding decrease in SAW oscillator frequency) until all reactive sites are consumed.

The selection of this model reactive polymer-vapor system was made on the basis of several factors. The poly(maleate ester) structure is closely related to maleic anhydride which is a very reactive dieneophile. Cyclopentadiene is a very volatile compound and reacts vigorously with maleic anhydride. The cis double bond as well as the ester linkage in the polyester chain impart a soft, rubbery character to the polymer which should permit rapid permeation of cyclopentadiene vapor. Many Diels-Alder adducts undergo a retro Diels-Alder reaction which would allow reversible operation

of the detector. Finally, the simple chemical structure facilitates spectroscopic interpretation of structural changes.

The approach used in this study was to first synthesize and characterize poly(ethylene maleate) and then to verify that the Diels-Alder addition of cyclopentadiene under heterogeneous vapor-solid conditions proceeds in a similar specific, rapid and neat quantitative manner as is known to occur in a homogeneous condensed system. Parallel experiments were also conducted on maleic anhydride and dimethylmaleate model compounds to provide spectroscopic analytical information about the polymeric Diels-Alder adduct. The solubility parameter of PEM was determined in order to investigate possible correlations with the solubility parameter and the permeability of various vapors exposed to PEM. Determination of the SAW vapor sensor performance was obtained by measuring SAW frequency shifts of a device coated with a PEM film and exposed to several concentrations of cyclopentadiene and other vapors of varying solubility parameter. A final experiment was conducted using a poly(isoprene) film with *n*-phenylmaleimide mixed into it, in order to ascertain the importance of having the selective receptor covalently bonded to the film matrix as opposed to having the receptor merely occluded in the film.



## EXPERIMENTAL SECTION

Reagents. Maleic anhydride (Eastman) was recrystallized from chloroform followed by sublimation under nitrogen at 1 atm. Ethylene glycol (Fisher) was dried immediately before use by azeotroping with toluene under nitrogen. Xylene (Fisher) was also dried immediately before use by azeotroping with toluene under nitrogen. p-Toluene sulfonic acid (Fisher) was used as received. Cyclopentadiene was prepared by cracking dicyclopentadiene at 170° under nitrogen(2). Dimethylmaleate (Pfaltz and Bauer) was distilled under nitrogen. Solvents, unless specified otherwise were certified reagent grade and used as received.

Apparatus. Infrared spectra were obtained with a Perkin-Elmer 267 grating infrared spectrophotometer from solvent evaporated film samples supported on NaCl discs or from KBr pellets. NMR spectra were obtained with a Varian EM390 NMR spectrometer from deuteriochloroform solutions referenced against tetramethylsilane. Differential scanning calorimetry and thermogravimetric analysis thermograms were obtained with a DuPont 910 DSC, 951 TGA and 990 thermal analysis unit under nitrogen atmosphere at a 10°C per min. heating rate. Molecular weight measurements were obtained with a Wescan 232A vapor pressure osmometer.

The surface acoustic wave device used in this study was fabricated on an ST-Quartz substrate (1.27cm x 5.04cm) and was designed to operate at 51 MHz. Details of the device and its supporting electronics are provided in an NRL Memorandum Report (1).

Vapor exposures of the coated SAW device were conducted in a 2000 ml, three neck, round bottom flask which was fitted with vapor tight glass stoppers (exposed rubber must be avoided since it results in organic vapor

absorption and subsequent slow evolution which causes baseline drift), electrical feedthroughs and a stirring bar as shown in figure 1. Samples were introduced in liquid form using a microliter syringe. The output of the SAW oscillator was connected to a FLUKE model 1910A frequency counter having a resolution of 0.1Hz, interfaced to an APPLE II microcomputer system which monitored and stored all experimental data.

Poly(ethylene maleate) Synthesis. Poly(ethylene maleate), PEM, was prepared by an acid catalyzed polyesterification. To a four neck 100 ml resin kettle fitted with a nitrogen inlet bubbler, thermometer and a Dean and Stark trap were added 15.52g (0.250 mol) ethylene glycol, 25 ml xylene and 6 ml toluene. The kettle was heated by a mantle until 7 ml were collected in the Dean and Stark trap. The mixture was cooled to 50°C and 24.51g (0.250 mol) maleic anhydride and 0.05g p-Toluene sulfonic acid were added. The mixture was refluxed under nitrogen for 11 hrs. Collection of water indicated conversion was nearly quantitative. The polymer mixture was cooled to 120°C, 0.01g hydroquinone was added and mixed to stabilize the unsaturated bonds, and the hot polymer was poured into a wide mouth jar. The PEM was purified by dissolving in chloroform and precipitating into diethyl ether. When this operation is done at room temperature, the polymer separates as a gum. Vacuum drying results in a large volume of foaming which collapses on removal of the vacuum. If the precipitation is carried out below -20°C, the PEM separates as a flocculant precipitate from which the supernate can easily be decanted. On warming the PEM becomes slightly gummy, however, much less foaming is observed on vacuum drying. The PEM should not be heated or partial chloroform insolubilization results.

Diels-Alder Adducts. The maleic anhydride-cyclopentadiene adduct, MA-CP, model compound was prepared by simply adding an excess of cyclopentadiene to

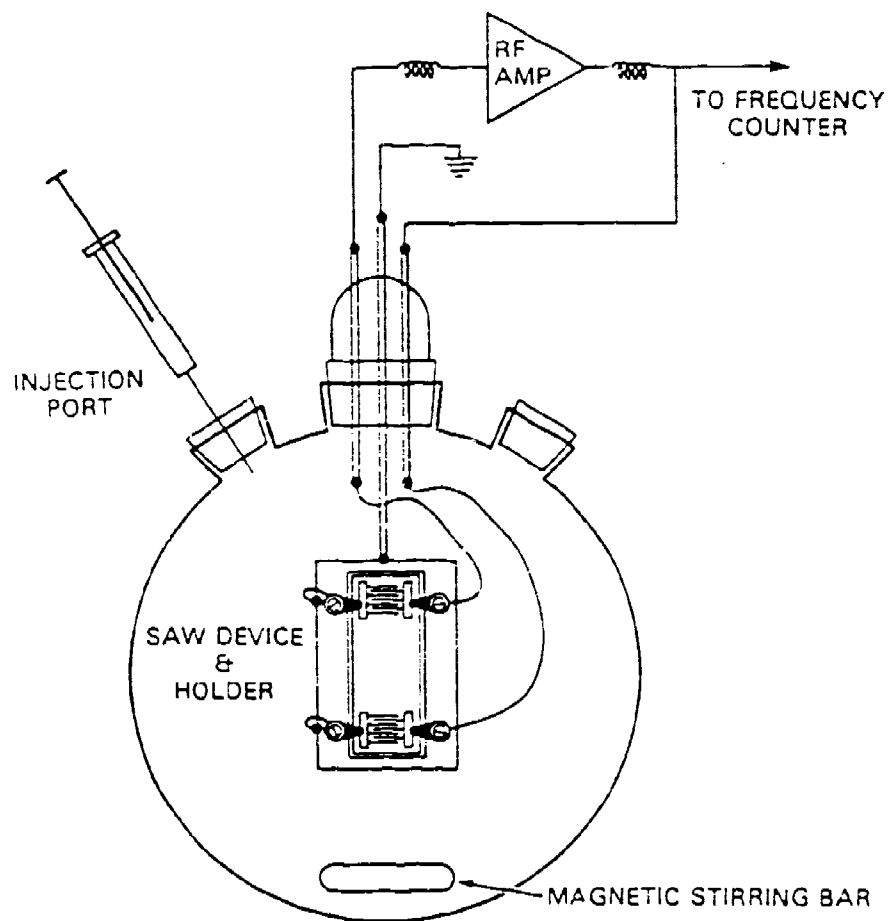


Figure 1. SAW device vapor exposure apparatus.

0.50g maleic anhydride in a 25 ml Erlenmeyer flask with external cooling(2). The product was recrystallized from ethanol, MP=165°C. The dimethyl maleate-cyclopentadiene adduct, DMM-CP, model compound was prepared by introducing 7.2g (0.050 mol) dimethylmaleate and 3.3g (0.050 mol) cyclopentadiene to the test tube liner of a 250 ml Parr bomb which was then charged with 1250 psi nitrogen and heated at 75°C with magnetic stirring for 24 hrs. The reaction mixture as worked up by distillation at reduced pressure, and a fraction collected at 90-91°C/1 torr was >98% pure by gas chromatography analysis. NMR and IR spectra were consistent with the assigned structure. This adduct could not be synthesized in good yield in an open system by refluxing in chloroform solution due to competitive formation of the cyclopentadiene dimer and escape of the cyclopentadiene. The N-phenylmaleimide-cyclopentadiene adduct, PMI-CP, was prepared by adding an excess of cyclopentadiene (2.00g) to 1.00g N-phenylimide in a 25 ml Erlenmeyer flask with external cooling. The product was recrystallized from methanol, MP=143°C.

While the reaction of cyclopentadiene with dimethylmaleate is slow, reaction with PEM is quite fast. The poly(ethylene maleate)-cyclopentadiene adduct, PEM-CP, is rapidly formed on mixing 0.50g PEM in 3.0g chloroform with 1.0g cyclopentadiene. The PEM-CP is isolated and purified by dropwise precipitation into diethylether cooled below -20°C under nitrogen followed by decantation and vacuum drying. Further purification is obtained by reprecipitation.

Molecular Weight Measurements. PEM and PEM-CP adduct molecular weight measurements by vapor pressure osmometry were made in 1,2-dichloroethane solution over a concentration range of 4 to 30g Polymer/Kg  $\text{CH}_2\text{ClCH}_2\text{Cl}$  solution at 35°C using benzil as a calibration compound. Both PEM and PEM-

CP occlude residual quantities of  $\text{CHCl}_3$  from the purification procedure, and it was found necessary to do a final reprecipitation from  $\text{CH}_2\text{ClCH}_2\text{Cl}$  to obtain a constant and reproducible molecular weight.

Solubility Parameter Determination. The PEM solubility parameter was obtained by gravimetrically measuring the swelling of a 30 to 40 mg quantity of PEM immersed in solvents of varying solubility parameter. Solvents included water, methanol, ethanol, 2-propanol, t-butanol, acetone, methylene chloride, tetrahydrofuran, benzene, ethylacetate, carbon tetrachloride, cyclohexane, diethylether and n-pentane.

PEM Film Preparation. Thin PEM films supported on SAW devices or on blank 2.5 x 7.5 cm microscope slides were prepared by spin coating at 1900 rpm. Solutions of PEM in chloroform ranging in concentration from 0.03 to 0.05g PEM/g solution yield films ranging from 0.5 to 2.0 micrometer in thickness as determined gravimetrically from the blank microscope slide. The PEM density is 1.353 g/cm<sup>3</sup>.

SAW Vapor Sensor Evaluation. Films of PEM were applied by spin coating onto a polished ST-quartz SAW device (1.27cm x 5.08cm) having gold interdigital transducers (50 electrode pairs, 100 micrometer wavelength) spaced 4.0 cm apart. A bead of silicone adhesive was applied to the ends of the device to minimize acoustic reflections. PEM films having a thickness of 0.69 micrometers were obtained by spinning at 1900 rpm for 1 minute from a chloroform solution having a concentration of 0.0317 gm. PEM per gm. solution. The devices were baked at 110°C for 5 minutes to drive off residual solvent. Films produced in this way reduced the resonant frequency of the SAW delay line oscillator by approximately 90 kilohertz when compared to an uncoated SAW device ( $f_0 = 31.346800 \text{ MHz}$ ). Coated devices were allowed

to stand in clean air for at least 12 hours prior to use since this procedure seemed to eliminate drift problems encountered when freshly coated devices were used immediately. Films of cis-poly(isoprene) mixed with N-phenylmaleimide were prepared on the SAW devices using a different procedure. Several drops of a chloroform solution containing N-phenylmaleimide and cis poly(isoprene) in a 1:1 ratio were coated onto the device and the solvent was allowed to evaporate. As before, the device was baked at 110°C for 5 minutes to drive off residual solvent. Frequency shifts of the SAW oscillator caused by vapor interaction with the coating film were obtained by injecting the sample into the 3 neck flask in liquid form using a microliter syringe. The volume injected determined the vapor concentration after complete volatilization had occurred. A magnetic stirring bar was used to insure homogeneity of the vapor mixture. All experiments were conducted at room temperature ( $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$ ) and atmospheric pressure.

## RESULTS AND DISCUSSION

Since this PEM coating-cyclopentadiene vapor model system is being used to obtain operational information and limitations of the SAW device as a vapor sensor, a detailed characterization of the chemical system was undertaken. This will allow correlation of the coating structure and coating-vapor interactions with the SAW device response. The characterization includes spectroscopic and thermal analyses, molecular weight measurements and solubility parameter determination. The SAW device response involves time dependent frequency response measurements of the PEM coated device to vapor exposures.

Infrared Spectra. The infrared spectra of PEM and of PEM-CP adduct are displayed in Figure 2a. The PEM spectrum exhibits the  $\alpha,\beta$ -unsaturated diester carbonyl stretch at  $1724\text{ cm}^{-1}$  and an aliphatic carbon-hydrogen stretch at  $2970\text{ cm}^{-1}$ . Absorptions corresponding to a symmetrical disubstituted ethylene appear at  $3080$ ,  $1641$  and  $980\text{ cm}^{-1}$ . The  $980\text{ cm}^{-1}$  band would correspond to a trans fumarate out of plane bending. NMR data also indicates a minor amount of fumarate structure suggesting that a minor amount of cis to trans isomerization occurs during the polymerization. After reacting with cyclopentadiene to form the PEM-CP adduct, the ethylenic absorptions at  $1641$  and  $980$  disappear, and a stronger ethylene carbon hydrogen stretching at  $3070$  appears. Also observed are a much stronger aliphatic absorption at  $2970\text{ cm}^{-1}$  and a carbonyl shift to  $1730\text{ cm}^{-1}$ . The changes are consistent with the bicyclic structure which includes a cyclic olefin band and an  $\alpha,\beta$ -saturated diester. An identical spectrum of the PEM-CP adduct may be obtained by simply evaporating a PEM film from a chloroform solution onto an NaCl disc followed by a 10 min. exposure to a saturated

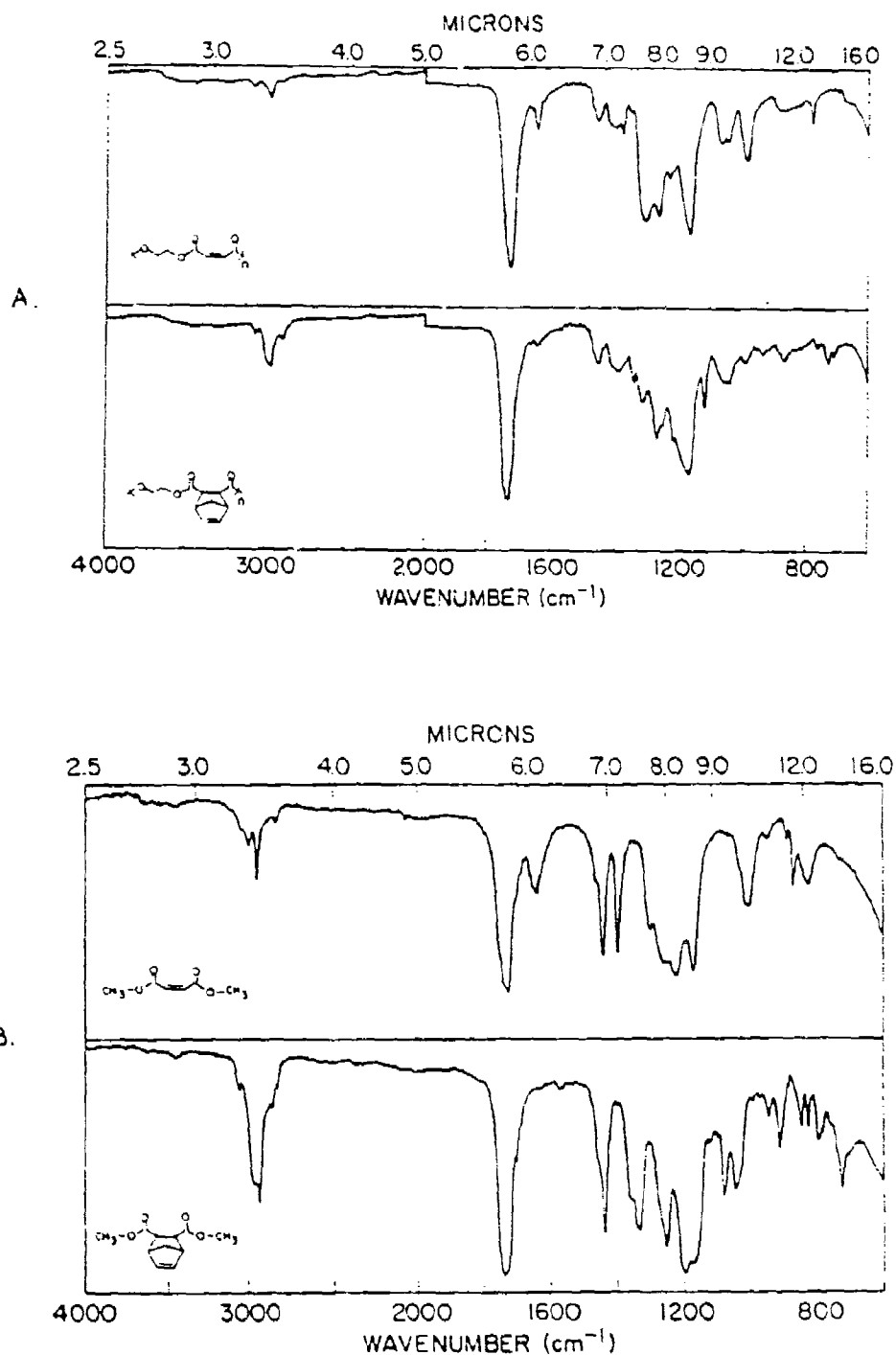


Figure 2. Infrared spectra of (a) poly(ethylene maleate) and the poly(ethylene maleate)-cyclopentadiene adduct and of (b) dimethylmaleate and the dimethylmaleate-cyclopentadiene adduct.



cyclopentadiene atmosphere which would indicate the adduct forming reaction is rapid and quantitative.

Model compound spectra of dimethylmaleate (DMM) and the DMM-CP adduct are presented in Figure 2b. Consistent with the polymeric system, conversion of DMM to the DMM-CP adduct results in disappearance of the  $1641\text{ cm}^{-1}$  DMM ethylenic band, a shift of the  $1729\text{ cm}^{-1}$   $\alpha,\beta$ -unsaturated carbonyl band to  $1739\text{ cm}^{-1}$  and a substantial increase in the intensity of  $2960$  aliphatic C-H stretching.

Heating the PEM-CP adduct film to temperatures as high as  $185^\circ\text{C}$  did not regenerate the original PEM film but a film with a spectrum indicative of other degradative changes was obtained.

NMR Spectroscopy. The NMR spectra of PEM and of PEM-CP are displayed in Figure 3a and 3b. The PEM spectrum consisted of three signals; a partially resolved multiplet at  $\delta = 4.45$  corresponding to the methylene protons and two singlets at  $\delta = 6.3$  and  $6.85$  corresponding to the vinyl protons. The intensity ratio of methylene proton signal to vinyl proton signals is 2:1 and would indicate that a partial isomerization of the cis maleate repeat unit to the trans fumarate unit had occurred during the polymerization. The spectrum of the PEM-CP adduct is interpreted with the aid of spectra for the cyclopentadiene adducts with the maleic anhydride (Figure 3c) and dimethyl maleate (Figure 3d) model compounds. The easiest identifiable feature is the signal at  $\delta = 1.5$  corresponding to the bridging methylene protons. Other proton assignments have been made as indicated in Figure 3. When a film of PEM is exposed to cyclopentadiene vapor, a spectrum of the dissolved polymer identical to that of Figure 3b is obtained. This observation is consistent with the infrared result of a rapid and quantitative adduct forming reaction.

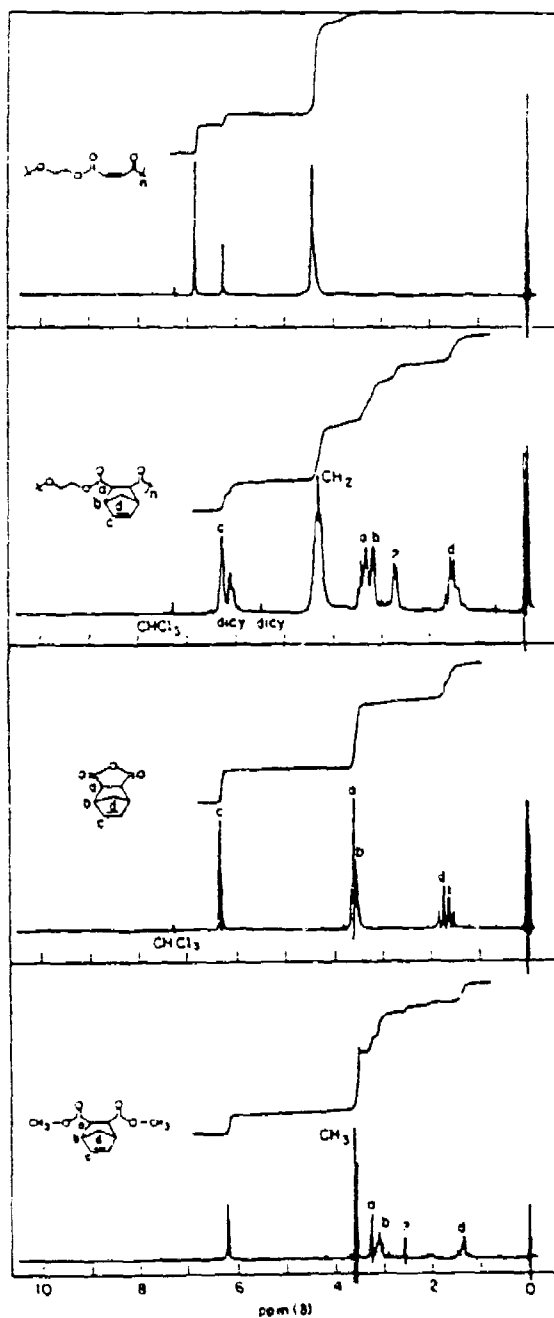


Figure 3. PMR spectra of (a) poly(ethylene maleate), (b) poly(ethylene maleate)-cyclopentadiene adduct, (c) maleic anhydride-cyclopentadiene adduct and (d) dimethylmaleate-cyclopentadiene adduct.

Molecular Weight. It was of interest to obtain a molecular weight measurement on this system as well as use the measurement to determine the degree of conversion to the Diels-Alder adduct. When PEM reacts with cyclopentadiene to form the adduct, a molecular weight increase proportional to the PEM-CP to PEM repeat unit would be predicted assuming a quantitative conversion. The molecular weight data is presented in Figure 4. The PEM number average molecular weight is 4520 which corresponds to 32 repeat units. The molecular weight of the PEM-CP adduct is 8250 which corresponds to 39 repeat units assuming quantitative addition of the cyclopentadiene to the PEM repeat unit. A possible source of greater than 1:1 stoichiometry would be addition of a second cyclopentadiene unit to some of the PEM-CP repeat units although we do not have other data at this time to support such a reaction. Another source would be a partial fractionation of the PEM-CP adduct to higher molecular weights during the precipitation purification operation to separate the polymer adduct from absorbed cyclopentadiene and dicyclopentadiene byproduct. In a simple gravimetric experiment, where a thin film of PEM coated onto a microscope slide was exposed to a saturated atmosphere of cyclopentadiene followed by evacuation, the ratio of exposed film weight to initial film weight was 1.25. If the uptake is quantitative, this ratio should correspond to the ratio of the PEM-CP repeat unit to the PEM repeat unit molecular weight which is 1.47.

Also noteworthy in Figure 4 is the difference in polymer-solvent interaction between PEM and PEM-CP as reflected in the negative and positive slopes. This indicates that in a reactive polymer-vapor system, a change in the medium or reactive polymer occurs, and caution should be exercised in interpreting kinetic data.

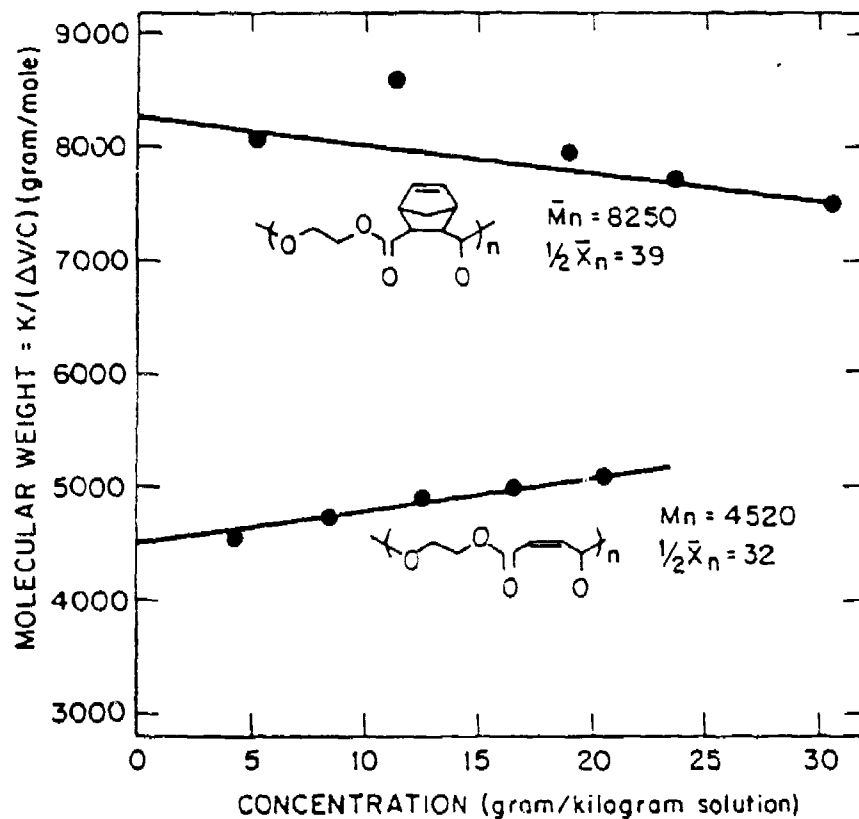


Figure 4. Vapor pressure osmometry molecular weight measurements of poly(ethylene maleate) and the poly(ethylene maleate)-cyclopentadiene adduct in toluene solution at 63°C.

Thermal Analysis. Thermal analysis data were obtained to determine the change in glass transition temperature effected by PEM-CP adduct formation, and, if the adduct formation were reversible, at what temperature the retro-Diels-Alder reaction would occur. The DSC and TGA thermograms of PEM and PEM-CP are presented in Figure 5. Conversion of PEM to PEM-CP results in only a small Tg increase from  $-10^{\circ}$  to  $0^{\circ}\text{C}$ . At higher temperatures the PEM exhibited a weak endotherm at  $125^{\circ}\text{C}$  while the PEM-CP adduct displayed an exotherm at  $150^{\circ}\text{C}$ . TGA indicated this  $150^{\circ}\text{C}$  exotherm did not correspond to a rapid liberation of cyclopentadiene. When a sample of the PEM-CP adduct was heated to  $185^{\circ}\text{C}$  in the well of an evacuated IR gas cell only a trace of cyclopentadiene vapor was observed. This is consistent with the infrared experiment involving heating a PEM-CP adduct film as discussed earlier.

Similar analysis on the maleic anhydride model system showed a reverse Diels-Alder reaction while the dimethylmaleate system followed the behavior of the PEM-CP adduct.

Solubility Parameter. The solubility parameter was measured to determine the variation in PEM physical absorption of solvents and whether the selectivity would be paralleled by vapor phase detection measurements with the SAW device. The swelling data is presented in Figure 6. The PEM solubility parameter is  $9.7 \pm .5$  (cal/cm<sup>3</sup>), and the more polar solvents outside of this range are more strongly absorbed than the less polar solvents.

PEM Coated SAW Device Response to Cyclopentadiene Vapor. Injection of cyclopentadiene into the closed flask containing the coated SAW device resulted in a reduction of the oscillator frequency with time. Increasing the concentration of cyclopentadiene by repeated injections into flask resulted in corresponding increases in the rate of change of the oscillator

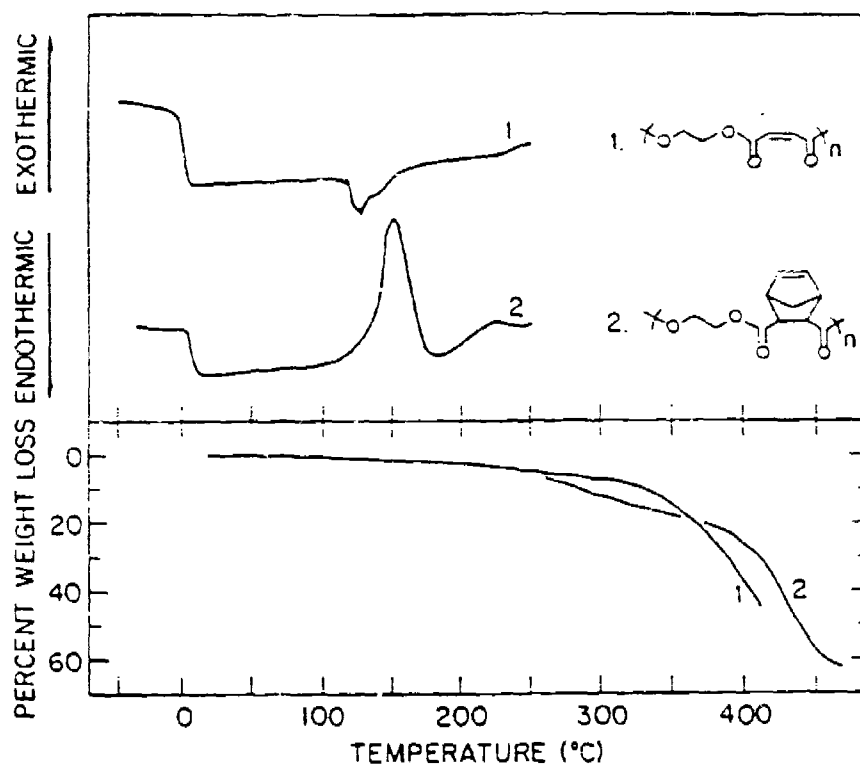


Figure 5. DSC and TGA thermograms of poly(ethylene maleate) and the poly(ethylene maleate)-cyclopentadiene adduct.

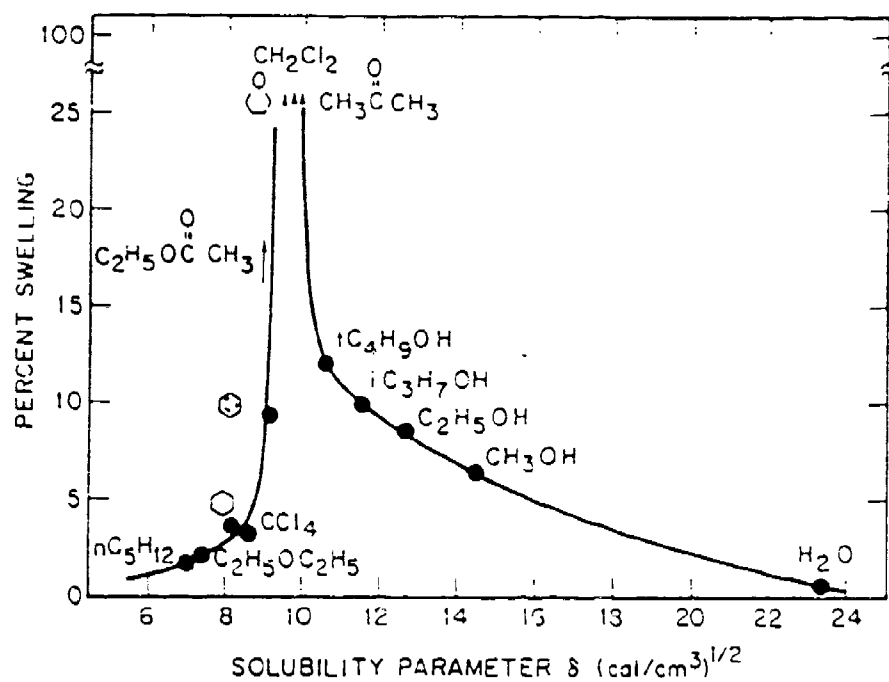


Figure 6. Poly(ethylene maleate) solubility parameter determination by solvent swelling measurements.

frequency. For example, at a concentration of 4000 ppm of vapor, the SAW device frequency dropped at a rate of 76.4 Hz per minute. After 10 minutes at this concentration an additional injection of cyclopentadiene was made to increase the vapor concentration to 5000 ppm whereupon the rate of frequency change increased to 89.9 Hz per minute. The rate at which the SAW device frequency decreased when exposed to various concentrations of cyclopentadiene is shown in Figure 7. The response is linear within experimental error over the concentration range investigated (i.e. 100 ppm to 10,000 ppm). The rate of the SAW frequency decreases is directly proportional to the rate of increase of mass of the coating film which is related to the Diels-Alder adduct formation rate. Thermal studies indicated that the retro Diels-Alder reaction did not occur significantly even at elevated temperatures. Thus, the sensor was considered to be completely irreversible. Upon flushing the system with clean air it was observed that the SAW frequency increased, indicating a significant loss of weight by the film. Continued flushing resulted in a stable SAW frequency which typically was about 40% less than the maximum frequency shift observed. For example, if the total cyclopentadiene exposure had shifted the SAW device resonant frequency down by 10 KHz, then flushing with air could cause the frequency to increase by about 4 KHz. It is believed that this partial reversibility is a result of outgassing of cyclopentadiene which had permeated into the regions of the PEM film where the Diels-Alder adduct had already formed.

The slope of the curve describing the rate of frequency change versus cyclopentadiene concentration was -0.019 Hz/ppm-min. The average baseline noise observed in these experiments was less than 2Hz rms measured over a 1 minute interval. Thus, the minimum detectable quantity for a 2:1 signal to noise ratio and a 1 minute observation time is about 200 ppm. However, the



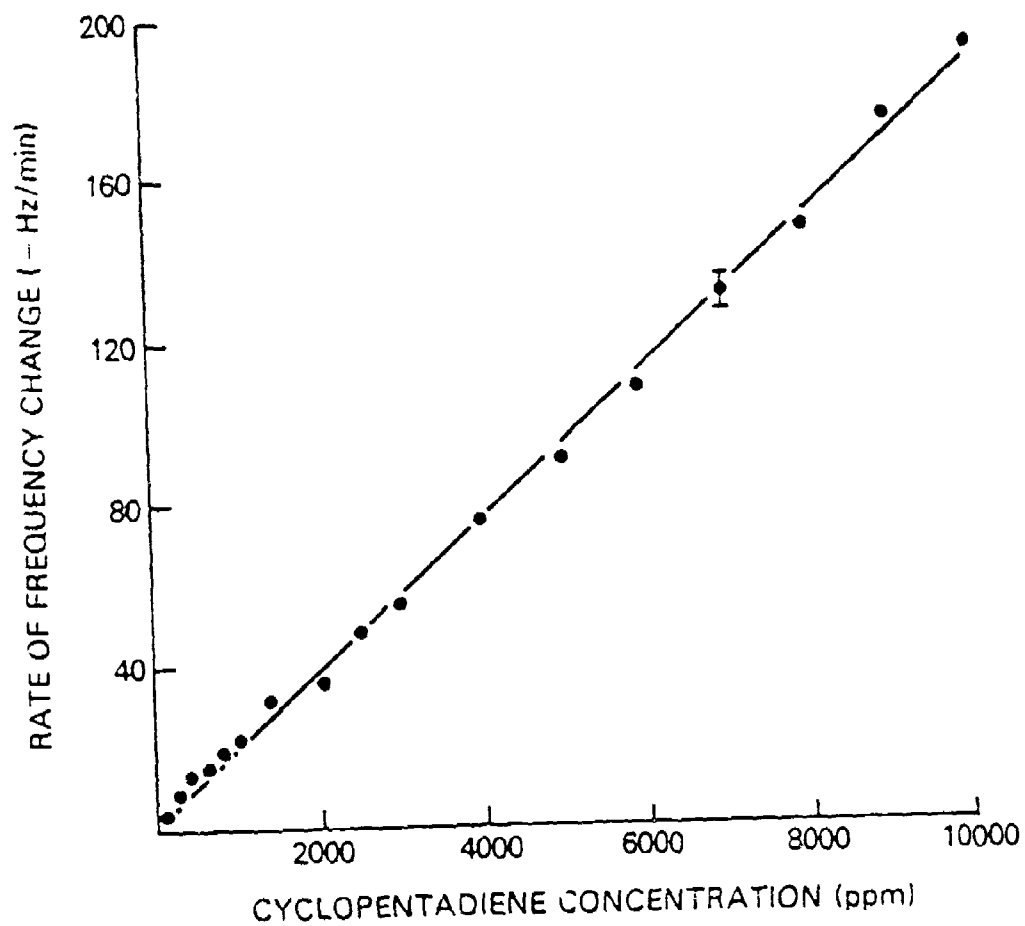


Figure 7. Response of PEM coated SAW device to various cyclopentadiene vapor concentrations.

nonreversible nature of the Diels-Adler adduct can be used to extend the detection limits much lower by increasing the exposure time. In this way the film behaves as a chemical dosimeter, integrating the concentration of cyclopentadiene exposure with time. While quantitative experiments to explore this possibility were not conducted, a qualitative observation of this effect was often made when the sample flask was not adequately cleaned after use. Early in these investigations, the sample flask was cleaned after being exposed to cyclopentadiene by rinsing with acetone followed by soap and water washing. Although clean to the sense of smell, reuse of the flask resulted in a steady downward baseline drift over a period of hours. The drift could only be eliminated by heating the flask in a bunsen burner prior to use. Thus, long term exposure to low concentrations of vapor results in a continuous, measurable mass increase of the film. If one assumes that a film whose mass produces a frequency shift of 100 KHz on a 31 MHz SAW oscillator can pick up 20% of its own mass in cyclopentadiene (i.e. 20 KHz) before it is exhausted, then the estimated life of such a dosimeter is in excess of 1700 hours when exposed to concentrations of cyclopentadiene around 10 ppm.

PEM Coated SAW Device Response to Various Vapors. The PEM coated SAW device was exposed to a variety of vapors to determine the selectivity of the film. 2000 ppm aliquots of vapor were prepared in the sample flask by syringe injection of volatile liquid and the response of the SAW oscillator frequency with time was recorded. The flask was purged with clean air for approximately 10 minutes after the sensor response leveled off. The cycle of injection, equilibration, and purge was repeated for samples of acetone, methylene chloride, benzene, methanol, pentane, and cyclopentadiene. The results are illustrated in Figure 8. All of the samples investigated except

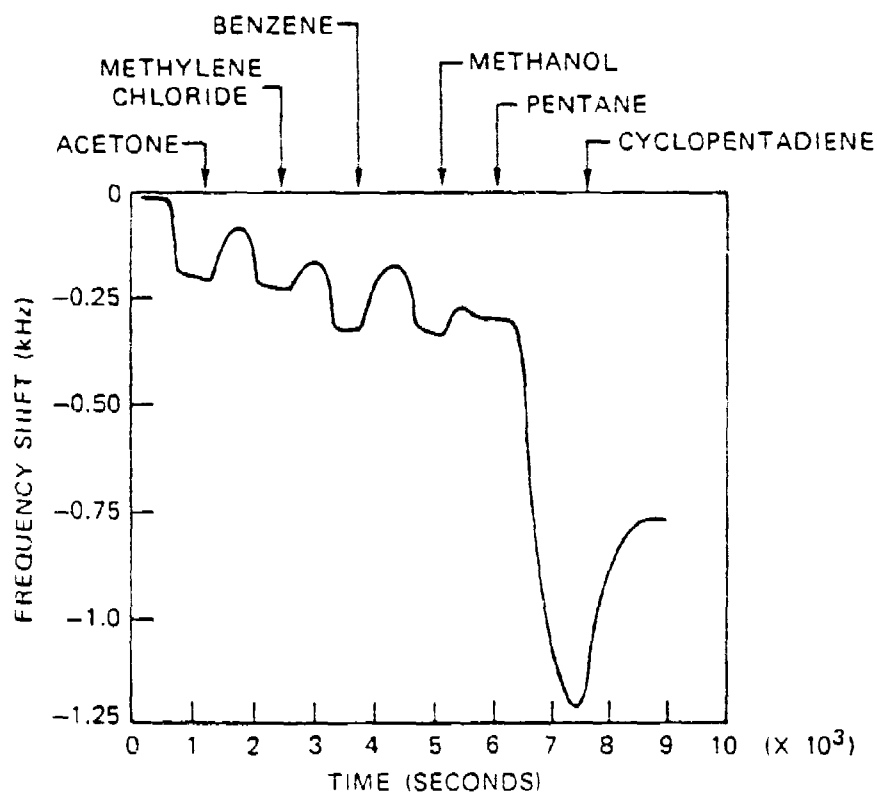


Figure 8. Response of PEM coated SAW device to 2000 ppm exposures of various vapors.

cyclopentadiene caused a response which leveled off quite rapidly after injection. The device response after exposure to cyclopentadiene never leveled off. Upon purging the sample flask the device frequency stopped its steady downward trend and returned to a level which was significantly below that at which it started. The results obtained from solvent vapor exposures are consistent with those expected of non-reactive vapors which permeate the film. The concentration of vapor in the film quickly reaches equilibrium with the concentration of vapor in the flask. Removal of the vapor in the flask allows the removal of vapor from the film. Thus, the reversible SAW frequency shift observed is simply a result of the physical sorption of the vapor causing an increase in the effective mass of the film. The device response to cyclopentadiene vapor exhibits both reversible and non-reversible components. As described previously, the reversible component of the response is probably due to unreacted cyclopentadiene outgassing from the film. The formation of the Diels-Alder adduct is responsible for the non-reversible component of the response.

It is well known from chromatography (see, for example, reference 5) that a volatile solute vapor can dissolve in a non-volatile solvent coating. The resulting equilibrium can be described by a partition coefficient for a non-ideal solution (5):

$$K = \frac{RT}{M_1 \gamma p_2} \quad (1)$$

where K is the partition coefficient defined as the ratio of the weight of solute vapor per gram of solvent coating to the weight of solute vapor per cm<sup>3</sup> of vapor volume at the system temperature. R is the gas constant; T is the temperature of the system; M<sub>1</sub> is the molecular weight of the solvent coating; p<sub>2</sub> is the vapor pressure of the solute gas at the system

temperature; and  $\gamma$  is the activity coefficient for the solute/solvent system. For regular solutions, the activity coefficient is related to the solubility parameters of the solute and solvent through the following relationship (6):

$$\ln \gamma = \frac{\Delta H_{\text{mix}}}{RT} = \frac{\bar{V}_2 (\delta_1 - \delta_2)^2}{RT} \quad (2)$$

where  $\delta_2$  is the solubility parameter of the solute vapor;  $\delta_1$  is the solubility parameter of the solvent film; and  $\bar{V}_2$  is molar volume of the vapor. This can be combined with equation 1 to yield:

$$K = \frac{RT}{M_1 p_2 \exp \left( \frac{\bar{V}_2 (\delta_1 - \delta_2)^2}{RT} \right)} \quad (3)$$

While this expression is rigorously correct only for regular solutions, it does offer significant qualitative insight even when the solvent is a permeable polymeric film. If one is interested in comparing the relative magnitudes of the partition coefficient for various vapors in the same coating film and at the same temperature then equation 3 can be simplified to:

$$K_{\text{rel}} = \frac{1}{p_2 \exp \frac{\bar{V}_2 (\delta_1 - \delta_2)^2}{RT}}$$

since  $R$ ,  $T$ , and  $M_1$  are constants. The values for the relative partition coefficient for the various vapors investigated are tabulated along with the experimentally measured frequency shift in Table I. A system temperature of 300°K and a solubility parameter of 9.7 (cal/cm<sup>3</sup>) for PEM are assumed. Vapor pressures were obtained from reference 4. Solubility parameters were obtained from reference 3. The results in parenthesis presented in Table I have been normalized to acetone to allow an easier comparison. Calculated

TABLE I

Measured Frequency Shifts and Calculated Relative Partition  
Coefficients for Various Vapors in PEM

Vapor	$\frac{5}{2} (\text{Cal}/\text{Cm}^3)^{1/2}$	$\Delta f$ (Hz)	$K_{\text{rel}}$ Units
Acetone	10.0	-166 (1.0)	3.4 (1.0)
Methylene Chloride	9.7	-117 (0.7)	1.6 (0.47)
Benzene	9.2	-162 (0.98)	9.0 (2.6)
Methanol	14.5	-137 (0.83)	3.0 (0.88)
n-Pentane	7.0	- 16 (.10)	0.4 (0.12)

(values in parenthesis are normalized to acetone)

values for the relative partition coefficient predict that the following order of frequency shift should be observed: Benzene > Acetone > Methanol > Methylene Chloride > n-Pentane. Experimentally, the following order of frequency shifts was observed: Acetone > Benzene > Methanol > Methylene Chloride > n-Pentane. Agreement between theory and experiment is qualitatively and quantitatively good except for Benzene. The reason for this discrepancy is not known.

Poly(isoprene) - Phenylmaleimide Coated SAW Device Response. To determine whether chemical bonding of the vapor reactive functional group to the polymer matrix was required for selective detector response, a simple dienophile was occluded in a cis-polyisoprene matrix and tested for cyclopentadiene sensitivity. Maleic anhydride was not suitable for this experiment since it evaporated from a 50 weight percent polyisoprene film in 20 minutes. Substitution of N-phenylmaleimide which has Diels-Alder reactivity comparable to maleic anhydride, solved the evaporation problem. However, the spin coating technique could not be used to apply the N-phenylmaleimide occluded polyisoprene film. Spectroscopic analysis of films prepared in this manner showed that no N-phenylmaleimide was retained in the film. This was confirmed by the lack of a detector response of the SAW sensor. When a film was prepared by evaporation of a 1:1 N-phenylmaleimide-polyisoprene solution in chloroform, a detector response of magnitude comparable to the PEM film was obtained. This experiment indicates that covalent bonding of the vapor receptor of moiety to the polymer matrix is not necessary for detector sensitivity. However, it is necessary if the spin coating technique of application is used.

### CONCLUSION

A SAW delay line oscillator coated with a film of poly(ethylene maleate) has been shown capable of detecting cyclopentadiene vapor in a highly selective and sensitive manner. Both the sensitivity and selectivity of the microsensor are determined primarily by the coating film. In this study, the selectivity was high due to the specificity of the Diels-Alder reaction between the cyclic diene vapor and the dienophile coating. Sensitivity was determined largely by the rate at which the vapor reacted with the coating since the reaction was irreversible. Coating films which react more rapidly are desirable so that low concentrations of vapor will provide a larger mass change in a shorter period of time. Thus, the dosimeter would be able to sense the presence of lower vapor concentrations for a given exposure time.

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### BRIEF

The behavior of a surface acoustic wave chemical microsensor has been investigated using the Diels-Alder reaction between poly(ethylene maleate) and cyclopentadiene as a model selective polymer-vapor system.



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